

# PATENT ABSTRACTS OF JAPAN

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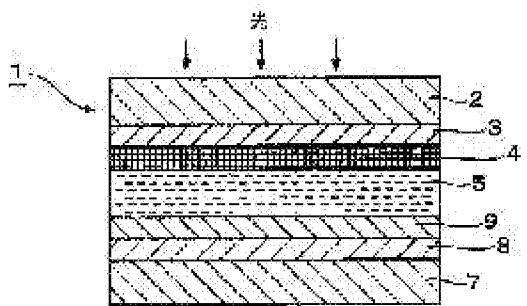
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## (54) PHOTOELECTRIC TRANSFER ELEMENT

### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a photoelectric transfer element which has a new structure that has improved greatly the photoelectric transfer efficiency by suppressing the loss arising from internal resistance of the current collector electrode.

SOLUTION: The photoelectric transfer element comprises at least a pigment- carrying semiconductor layer, a current collector electrode, an electrolyte layer, and a counter electrode between two sheets of substrates, of which at least one is made of a light-transmitting material. On one face of the substrate made of light-transmitting material, the pigment-carrying semiconductor layer is provided, and on the other face of the pigment-carrying semiconductor layer, the porous current collector electrode is provided. On one face of the other substrate, the counter electrode is provided and the electrolyte layer is provided between the above current collector electrode and the counter electrode.



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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to an optoelectric transducer. More particularly, this invention relates to the optoelectric transducer which has a new structure whose photoelectric conversion efficiency expressed with the ratio of a cell output to incident light quantity improved by leaps and bounds.

#### [0002]

[Description of the Prior Art] For example, optoelectric transducers, such as a solar cell, are dramatically expected as a clean energy source, and the pn junction type solar cell etc. are already put in practical use. However, since said silicon system solar cell uses a highly pure material as a raw material or needs a high temperature process and a vacuum process of about 1000 \*\*, reduction of the manufacturing cost has been a big technical problem. Then, the solar cell which performs charge separation according to the electric potential gradient produced in the solid-liquid interface which does not need comparatively a highly pure material and a high energy process attracts attention in recent years.

[0003] When a semiconductor contacts metal, the Schottky barrier is made with the relation of the work function of metal and a semiconductor, but same junction can be performed also when the semiconductor and the solution have touched. In a solution, for example,  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ,  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ , When redox systems, such as  $\text{I}^-/\text{I}_2$ ,  $\text{Br}^-/\text{Br}^2$ , hydroquinone/quinone, are included, if an n-type semiconductor is soaked in a solution, the electron near the surface of a semiconductor will move to the oxidizer in a solution, and will reach an equilibrium situation. As a result, near the surface of a semiconductor is just charged and an electric potential gradient produces it. In connection with this, inclination arises also in the conducting zone and valence band of a semiconductor.

[0004] It is a wet solar cell which is going to carry out charge separation using this electric potential gradient, and it comprises a semiconductor electrode, a metaled counterelectrode, and a oxidation reduction solution. If the mechanism irradiates the surface of the semiconductor electrode soaked in the oxidation reduction solution, light with the energy more than the band gap of a semiconductor is absorbed, and near the surface, an electron will be generated to a conducting zone and it will generate an electron hole to a valence band. The electron excited by the conducting zone is transmitted to the inside of a semiconductor by the electric potential gradient which exists near the surface of the semiconductor mentioned above, and, on the other hand, the electron hole generated by the valence band takes an electron from the reduced form in a

oxidation reduction solution.

[0005] If a metal electrode is dipped in a oxidation reduction solution and a circuit is made between a metal electrode and a semiconductor, the reduced form from which the electron was taken in the electron hole will diffuse the inside of a solution, will receive an electron from a metal electrode, and will be returned again. This cycle is repeatable, a semiconductor electrode can be committed as a negative electrode, a metal electrode can be committed as an anode, respectively, and electric power can be supplied to the exterior. Therefore, photoelectromotive force becomes a difference of the oxidation reduction level of a oxidation reduction solution, and the Fermi level in a semiconductor.

[0006] In order to enlarge photoelectromotive force, it is using the strong oxidation reduction solution of oxidizing power low [ \*\* oxidation reduction level ], and being able to make a big difference, namely, using a semiconductor with a large band gap between \*\* oxidation reduction level and the Fermi level in a semiconductor.

[0007] However, if the oxidizing power of a oxidation reduction solution is too large not much, an oxide film is formed in a semiconductor's own surface, and photoelectric current is stopped in the inside of a short time. Since there is a problem which a band gap generally tends to dissolve into a solution about a band gap by the current through which a semiconductor of 3.0 eV or less flows in the case of photoelectric conversion, although the semiconductor of more than 3.0 eV is used, a band gap, A strong peak is too large for absorbing the sunlight near 2.5 eV efficiently. Therefore, since the visible range which occupies most sunlight cannot be absorbed at all but only an ultraviolet region can be absorbed, photoelectric conversion efficiency becomes very low.

[0008] As mentioned above, when a wet solar cell tries to perform photoelectric conversion, if the small semiconductor of a band gap is used, efficiency will improve, but the dissolution of an electrode takes place easily and a life falls. Conversely, although a life increases in a semiconductor with a large band gap, only the light of short wavelength is absorbed but efficiency is low. Then, the trial which a band gap tends to absorb to the light of long wavelength with coloring matter taking advantage of the stability of a large semiconductor was performed. This is called dye-sensitized solar cell. That is, the coloring matter which absorbs light on the surface of a semiconductor electrode tends to be made to stick to a dye-sensitized solar cell, and it tends to absorb the visible light of long wavelength with coloring matter from the band gap of a semiconductor electrode.

[0009] A different place from the conventional wet solar cell is having increased the light which performs not only a semiconductor but the organic coloring matter applied to the surface, and absorbs the absorption of light. The electron in the coloring matter excited by light is poured in into a semiconductor from a semiconductor surface. The coloring matter which oxidized by electron transfer is returned by the reduced form of a oxidation reduction solution. The other mechanism is the same as the wet solar cell from the former, the electron poured in into the semiconductor is picked out from a back plate, and the reduced form of the oxidized oxidation reduction solution is returned with a mated counterelectrode.

[0010] A dye-sensitized solar cell is related with photosynthesis, and is caught in many cases. Although chlorophyll was considered like photosynthesis as coloring matter at the beginning, unlike the natural chlorophyll exchanged for continuously new chlorophyll, there is a problem in respect of stability, and the photoelectric conversion efficiency as a solar cell is not filled with the coloring matter used for a solar cell to 0.5%, either. It is dramatically difficult to imitate the process of photosynthesis of a nature as it is, and to

constitute a solar cell.

[0011]Thus, although a dye-sensitized solar cell obtains a hint from photosynthesis and it is said that it would absorb the visible light of long wavelength, since the electronic transmission machine style became complicated actually, increase of the loss became a problem on the contrary. The absorption-of-light efficiency of the monomolecular layer supported by the surface is not filled to 1%, either. If the layer which absorbs light is thickened, absorption efficiency can be raised in a solid solar cell. However, about a dye-sensitized solar cell, only the monomolecular layer on the surface can pour an electron into a semiconductor electrode. Therefore, in order to lose the useless absorption of light, the coloring matter on a semiconductor surface is about [ with desirable considering it as a monomolecular layer ].

[0012]And in order to pour in the electron in the excited coloring matter into a semiconductor efficiently, having combined with the semiconductor surface chemically is preferred. For example, in order to combine with a semiconductor surface chemically about titanium oxide, it is important that coloring matter has a carboxyl group etc.

[0013]The group of Fujihira and others did the important improvement about this point. They have reported to the magazine Nature that photoelectric current became 10 or more times of the conventional adsorption process in 1977, when the carboxyl group of rhodamine B carries out an ester bond to the hydroxyl group of the  $\text{SnO}_2$  surface. It is since this has the pi orbital nearer than the conventional amide bond in which the electron in which the direction of the ester bond absorbed luminous energy within coloring matter exists on the surface of a semiconductor.

[0014]However, the electron which is in a conducting zone even if it is able to pour an electron into a semiconductor effectively has a possibility of recombining with the ground level of coloring matter, a possibility of recombining with a oxidation reduction substance, etc. Since there was such a problem, photoelectric conversion efficiency was still low in spite of the above-mentioned improvement about electron injection.

[0015]As mentioned above, it is that only the sensitizing dye supported with the monolayer by the semiconductor surface can pour in an electron to a semiconductor as a big problem of the conventional dye-sensitized solar cell. That is, the usable area with which it is smooth in the surface, and the single crystal or polycrystalline semiconductor which were used well [ until now ] to a semiconductor electrode do not have fine pores in an inside, but sensitizing dye is supported is equal to an electrode area, and there are few holding amounts of sensitizing dye.

[0016]Therefore, when such an electrode is used, the sensitizing dye of the monomolecular layer supported by the electrode can be absorbed 1% or less of incident light also on maximal absorption wavelength, but the utilization efficiency of light gets very bad. In order to heighten light-harvesting power, the trial which makes sensitizing dye a multilayer is also proposed, but sufficient effect is not acquired generally.

[0017]GURETTSUERU porosity-izes a titanium oxide electrode as a means to solve such a problem, Sensitizing dye was made to support and the internal surface product was increased remarkably (for example, refer to B.Oregan, M.Gratzel, Nature, 353,737 (1991), and JP,1-220380,A). This titanium oxide porous membrane is produced by a sol gel process, membranous porosity is about about 50%, and the nano porous structure which has very high specific surface area is formed. For example, in 8-micrometer thickness, a roughness factor (real area inside the porosity over a substrate area comparatively) amounts also to about 720. When this surface is calculated geometrically, the concentration of sensitizing dye will

reach  $1.2 \times 10^{-7}$  mol/cm<sup>2</sup>, and about 98% of incident light will be absorbed very much on maximal absorption wavelength.

[0018]The new dye-sensitized solar cell called this GURETSUERU cell is the feature that the point which absorbed efficiently increase of the fast holding amount of the sensitizing dye by porosity-izing of above-mentioned titanium oxide and sunlight, and sensitizing dye with it developed is big. [ a remarkable electron injection speed to a semiconductor and ] [ quick ]

[0019]GURETSUERU and others developed the bis(bipyridyl)Ru(II) complex for the dye-sensitized solar cell. The Ru complex has the structure of general formula \*\*\*\*- X<sub>2</sub> bis(2,2'-bipyridyl 4, 4'-dicarboxylate)Ru(II). X is Cl-, CN-, and SCN-. Fluorescence, visible optical absorption, and electrochemical and research systematic about a photooxidation reductive action were done about these. having the performance which boiled markedly \*\*\*\*-(diisocyanate)-bis(2,2'-bipyridyl 4, 4'-dicarboxylate)Ru(II) as a sunlight absorbent and a dye sensitizing agent, and was excellent was shown among these.

[0020]The visible optical absorption of this dye sensitizing agent is the charge transfer transition from metal to a ligand. The carboxyl group of a ligand is directly configurated in surface Ti ion, and forms close electronic contact between a dye sensitizing agent and titanium oxide. It is supposed that re-capture of the electron poured in to the conducting zone of titanium oxide by the dye sensitizing agent in which the electron injection from a dye sensitizing agent to the conducting zone of titanium oxide happened at a very quick speed of 1 pico second or less, and that opposite direction oxidized by this electronic contact is happened to the order of a microsecond. This speed difference produces the directivity of a photoexcited electron, and charge separation is a reason performed at very high efficiency. And this is the difference from the pn junction solar battery which performs charge separation according to the electric potential gradient of a pn junction surface, and it is prodigal and is the essential feature of a TSUERU cell.

[0021]Drawing 7 is a mimetic diagram showing the section structure of the cell of the dye-sensitized solar cell indicated to B.Oregan shown above, M.Gratzel, Nature, and 353,737 (1991). In drawing 7, the numerals 71 show the current collection electrode by which the glass substrate was provided in the numerals 72 on the undersurface of the glass substrate 71, respectively. Light enters from the upper surface side of the glass substrate 71. As the current collection electrode 72, since a photoelectric conversion layer exists in the current collection electrode lower part, a transparent conducting film like a tin-oxide film is used. The numerals 73 show the semiconductor layer which supported coloring matter. The semiconductor layer 73 takes the porous structure in the state where the semiconductor particles which particle diameter becomes from titanium oxide of about 50 nm or less etc. sintered to the current collection electrode 72. The numerals 74 show an electrolytic solution, and they are provided so that the semiconductor layer 73 which supported said coloring matter may be permeated. The numerals 75 show a Pt film. This Pt film is provided on the transparent conducting film 76 on the glass substrate 77.

[0022]The dye-sensitized solar cell which consists of the above-mentioned composition performs photoelectric conversion by the following mechanisms of action. First, in the sensitizing dye which passed along the current collection electrode with glass and translucency, was absorbed with the sensitizing dye which stuck to the semiconductor, and absorbed sunlight, an excitation electron generates the light which entered into the dye-sensitized solar cell. The excitation electron by which it was generated moves to the conductor of a semiconductor, is transmitted to between the sintered semiconductor particles, and reaches a negative electrode. The coloring matter which lost the excitation electron returns an electron from the

electrolyte of reduced condition to the state of receipt origin among the oxidation reduction objects included in an electrolysis solution. The oxidation reduction object included in the electrolysis solution which lost the electron and was in the oxidation state receives an electron from a counter electrode with a Pt film, and returns to reduced condition. The term of the "current collection electrode" used on these specifications means the electrode which exists in the form which touches the semiconductor formed in order to pick out outside the electron poured in into the semiconductor from coloring matter efficiently.

[0023]In a dye-sensitized solar cell, the internal resistance produced in the interface of the current collection electrode and semiconductor membrane which consist of transparent conducting films, and the interface of semiconductor particles becomes a conversion efficiency fall factor of a solar cell. Therefore, after applying the solution which distributed semiconductor particles to the glass substrate with a current collection electrode which consists of transparent conducting films generally, carrying out elevated-temperature sintering, avoiding isolation of semiconductor particles, and securing an electron transport pathway is performed.

[0024]However, in the aforementioned method, resistance of the current collection electrode which consists of transparent conducting films with the heat applied at the time of calcination goes up, and it becomes a conversion efficiency fall factor of a solar cell. Here, if thickness of the current collection electrode which consists of transparent conducting films is enlarged, the loss by said resistance can be reduced, but the photoelectric conversion degradation of the solar cell by the transmissivity of a transparent conducting film newly decreasing poses a problem.

[0025]As a current collection electrode material, from a viewpoint of reducing the ohm loss of the current collection polar zone, Resistivity is still lower than a transparent conducting film, and the thing which resistivity does not rise with the heat at the time of calcination, either, for example, is chosen from the group which consists of Au, Pt, Ag, Cu, aluminum, nickel, Zn, Ti, and Cr and in which the element more than a kind is contained at least is good. In the composition of drawing 7, a current collection electrode From an old transparent conducting film to however, Au. When it transposes to the electrode material which is chosen from the group which consists of Pt, Ag, Cu, aluminum, nickel, Zn, Ti, and Cr and with which the element more than a kind is contained at least, the problem on which the light volume which reaches a photoelectric conversion layer according to the transmissivity of an electrode material being low decreases remarkably arises. Therefore, said electrode material was not used as a current collection electrode which fixes semiconductor particles.

[0026]

[Problem(s) to be Solved by the Invention]Therefore, the purpose of this invention is to provide the optoelectric transducer which has a new structure whose photoelectric conversion efficiency improved by leaps and bounds by controlling the loss produced with the internal resistance of a current collection electrode.

[0027]

[Means for Solving the Problem]At least one side said technical problem between two substrates which consist of raw materials of a light transmittance state, In an optoelectric transducer which has a coloring matter support semiconductor layer, a current collection electrode, and an electrolyte layer and a counter-electrode at least, A coloring matter support semiconductor layer is allocated on one field of a substrate which consists of said light transmittance state raw material, a perforated current collection electrode is

allocated on a field of another side of this coloring matter support semiconductor layer, a counter-electrode is allocated on one field of a substrate of another side, and an optoelectric transducer to which an electrolyte layer exists between said perforated current collection electrode and a counter-electrode is solved.

[0028]In an optoelectric transducer of this invention, a current collection electrode which has many breakthroughs is used as a current collection electrode. The electrolytic solution of an electrolyte layer can contact a coloring matter support semiconductor layer provided in the acceptance surface side of a transparent substrate via a breakthrough provided in a current collection electrode.

[0029]

[Embodiment of the Invention]Hereafter, an example of the optoelectric transducer of this invention is explained concretely, referring to drawings. Drawing 1 is an outline sectional view of an example of the optoelectric transducer of this invention. In the optoelectric transducer 1 of this invention, the coloring matter support semiconductor layer 3 is allocated on one field of the transparent substrate 2 of a light transmittance state as illustrated. The perforated current collection electrode 4 is allocated in the field of another side of this coloring matter support semiconductor layer 3. At the point that an allocation order of the coloring matter support semiconductor layer 3 to the transparent substrate 2 and the current collection electrode 4 is reverse, the optoelectric transducer of this invention is deterministically different from the conventional optoelectric transducer shown in drawing 7. The substrate 7 of another side consists of a raw material of a light transmittance state or light impermeability nature, and the conducting film 8 and Pt film 9 used as a counter-electrode are allocated on the field of one of these. And the electrolyte layer 5 which consists of electrolytic solutions exists between this Pt film 9 and the perforated current collection electrode 4.

Therefore, the electrolytic solution can contact the coloring matter support semiconductor layer allocated in the acceptance surface side of a transparent substrate via the breakthrough of the current collection electrode 4 free.

[0030]The optoelectric transducer of the structure which established the place of photoelectric conversion in the acceptance surface side of a current collection electrode is indicated to JP,10-112337,A. However, in the structure of the optoelectric transducer indicated to JP,10-112337,A, since the electrolysis solution layer which has absorption in visible light exists in the acceptance surface side of a current collection electrode, there is a light transmission loss by an electrolysis solution by the time incident light reaches a photoelectric conversion layer. On the other hand, since the electrolysis solution which exists in the acceptance surface side of a current collection electrode is restricted to what has permeated the gap of the sintered semiconductor particles in the composition of this invention, the light transmission loss by an electrolysis solution until incident light reaches a photoelectric conversion layer is very small. It is using material with large reflectance for a current collection electrode in the composition of this invention, Since the semiconductor membrane which supported coloring matter with the form which can reuse the light which passed through the photoelectric conversion layer, and touches a current collection electrode exists, the influence of the light transmission loss by an electrolysis solution can be extremely inhibited also about reuse light.

[0031]Glass or a plastic can be used as the substrates 2 and 7. Since a plastic is flexibility, it is suitable for the use which needs pliability. The conducting film 8 laminated on the substrate 7 is a transparent or opaque thin film. As for the conducting film 8, metal, carbon (for example, platinum, gold, silver, copper, aluminum, rhodium, indium, etc.), or metallic oxides (tin oxide etc. which doped an indium tin multiple oxide and

fluoride) are mentioned. When the substrate 7 is a transparent substrate, the transparent thing of the conducting film 8 is also preferred.

[0032]Coloring matter support semiconductor layer 3 the very thing in the optoelectric transducer 1 of this invention can use the same thing as the coloring matter support semiconductor layer currently used by the conventional optoelectric transducer. By making coloring matter support, the semiconductor layer can obtain an optoelectric transducer with high photoelectric conversion efficiency. All can be used if it is coloring matter of daily use by the conventional dye sensitizing nature optoelectric transducer as coloring matter used in order to make a semiconductor layer support. Such coloring matter is publicly known to a person skilled in the art. Such coloring matter For example, RuL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> type a ruthenium \*\*\*\*-\*\* Aqua bipyridyl complex or ruthenium tris (RuL<sub>3</sub>), a transition metal complex a ruthenium screw (RuL<sub>2</sub>), male \*\*\*\*\*- tris (OsL<sub>3</sub>), and male \*\*\*\*\*-\*\*\*\* (OsL<sub>2</sub>) type -- or, Zinc-tetra(4-carboxyphenyl) porphyrin, an iron-hexacyanide complex, phthalocyanine, etc. are mentioned. As organic coloring matter, 9-phenyl xanthene dye, coumarin series coloring matter, an acridine dye, triphenylmethane dye, tetraphenylmethane system coloring matter, quinone system coloring matter, azo dye, an indigo pigment, cyanine dye, merocyanine system coloring matter, a xanthene dye, etc. are mentioned. Also in this, a ruthenium bis(RuL<sub>2</sub>)derivative is preferred. As a holding amount of the sensitizing dye to a semiconductor layer, what is necessary is just to be in the range of 10<sup>-8</sup> - 10<sup>-6</sup> mol/cm<sup>2</sup>, and 0.1 - 9.0x10<sup>-7</sup> mol/cm<sup>2</sup> is especially preferred.

[0033]As a material which forms a semiconductor layer, Cd, Zn, In, Pb, Mo, W, Sb, Bi, Cu, Hg, Ti, Ag, Mn, Fe, V, Sn, Perovskite like the oxide of Zr, Sr, Ga, Si, and Cr, SrTiO<sub>3</sub>, and CaTiO<sub>3</sub>, Or CdS, ZnS, In<sub>2</sub>S<sub>3</sub>, PbS, Mo<sub>2</sub>S, WS<sub>2</sub> and Sb<sub>2</sub>S<sub>3</sub>, Bi<sub>2</sub>S<sub>3</sub>, The sulfide of ZnCdS<sub>2</sub> and Cu<sub>2</sub>S, CdSe, In<sub>2</sub>Se<sub>3</sub>, The metal chalcogenide of WSe<sub>2</sub>, HgS, PbSe, and CdTe, other GaAs(es), Si, Se, Cd<sub>2</sub>P<sub>3</sub>, Zn<sub>2</sub>P<sub>3</sub>, InP, AgBr, Pbl<sub>2</sub>, Hgl<sub>2</sub>, and Bil<sub>3</sub> are preferred. Or the complex which is chosen from said semiconductor and which contains more than a kind at least, For example, CdS/TiO<sub>2</sub>, CdS/Agl, Ag<sub>2</sub>S/Agl, CdS/ZnO, CdS/HgS, CdS/PbS, ZnO/ZnS, ZnO/ZnSe, CdS/HgS, CdS<sub>x</sub>/CdSe<sub>1-x</sub>, CdS<sub>x</sub>/Te<sub>1-x</sub>, CdSe<sub>x</sub>/Te<sub>1-x</sub>, ZnS/CdSe, ZnSe/CdSe, CdS/ZnS, TiO<sub>2</sub>/Cd<sub>3</sub>P<sub>2</sub>, CdS/CdSeCd<sub>y</sub>Zn<sub>1-y</sub>S, and CdS/HgS/CdS are preferred. Especially, a support reaction with the aforementioned sensitizing dye advances more promptly by using an oxide for a semiconductor layer.

[0034]The thickness of the coloring matter support semiconductor layer 3 should just be the thickness of the range of 0.1-100 micrometers. When the thickness of the coloring matter support semiconductor layer 3 is less than 0.1 micrometer, sufficient photoelectric conversion effect may not be acquired. On the other hand, since the inconvenience of the permeability over visible light and a near infrared getting worse remarkably arises when thickness is more than 100 micrometers, it is not desirable.

[0035]The electrolyte layer 5 in the optoelectric transducer 1 of this invention consists of an electrolytic solution generated by dissolving an electrolyte in a solvent. An electrolyte usable to such a purpose will not be limited in particular, if the oxidation reduction system composition substance of the couple which consists of an oxidant and a reduced form is contained in the solvent, but the oxidation reduction system composition substance in which an oxidant and a reduced form have the same electric charge is preferred. The oxidation reduction system composition substance as used in an oxidation-reduction reaction in this specification means the substance of the couple which exists in the form of an oxidant and a reduced form reversibly. The

oxidation reduction system composition substance itself [ such ] is publicly known to a person skilled in the art. The oxidation reduction system composition substance which can be used by this invention For example, chlorine compound-chlorine, Iodine compound-iodine, bromine compound-bromine, thallium ion (III)-thallium ion (I), Mercury ion (II)-mercury ion (I), ruthenium ion (III)-ruthenium ion (II), Copper-ion (II)-copper-ion (I), iron ion (III)-iron ion (II), Vanadium-ions (III)-vanadium-ions (II), manganic acid ion permanganic acid ion, ferricyanide-ferrocyanide, quinone hydroquinone, fumaric acid-succinic acid, etc. are mentioned. Needless to say, other oxidation reduction system composition substances can also be used. Especially, iodine compound-iodine has it and as an iodine compound, [ preferred ] Especially iodination JIIMIDAZORIUMU compounds, such as iodination quarternary-ammonium-salt compounds, such as metal iodides, such as lithium iodide and potassium iodide, tetra alkylammonium iodide, and pyridiniumiodide, and iodination dimethylpropyl imidazolium, are preferred.

[0036]The solvent used in order to dissolve an electrolyte has the preferred compound which dissolved the oxidation reduction system composition substance and was excellent in ion conductivity. Although both an aqueous solvent and an organic solvent can be used as a solvent, since a oxidation reduction system composition substance is stabilized more, an organic solvent is preferred. For example, dimethyl carbonate, diethyl carbonate, methylethyl carbonate, Carbonate compounds, such as ethylene carbonate and propylene carbonate, Ester compounds, such as methyl acetate, methyl propionate, and a gamma butyrolactone, Diethylether, 1,2-dimethoxyethane, a 1,3-dioxosilane, Ether compounds, such as a tetrahydrofuran and 2-methyltetra hydra franc, Heterocyclic compounds, such as 3-methyl-2-OKISAZOJI linon and 2-methyl pyrrolidone, Aprotic polar compounds, such as nitril compounds, such as acetonitrile, methoxy acetonitrile, and propionitrile, sulfolane, JIJIME chill sulfoxide, and dimethylformamide, etc. are mentioned. These can also be used independently, respectively, and can also mix and use two or more kinds together. Especially, especially nitril compounds, such as heterocyclic compounds, such as carbonate compounds, such as ethylene carbonate and propylene carbonate, 3-methyl-2-OKISAZOJI linon, and 2-methyl pyrrolidone, acetonitrile, methoxy acetonitrile, and propionitrile, are preferred.

[0037]The electrode material used for the perforated current collection electrode 4 in the optoelectric transducer 1 of this invention has a preferred thing which is chosen from the group which consists of Au, Pt, Ag, Cu, aluminum, nickel, Zn, Ti, and Cr and which contains the element more than a kind at least. In order not to bar movement of the oxidation reduction object included in the electrolysis solution of the electrolyte layer 5 as a structure of the perforated current collection electrode 4, the structure of the mesh shape which can penetrate a fluid is preferred. The granularity in particular of the eye of a mesh shape electrode itself is not limited. What is necessary is just to have the granularity of sufficient eye required to enable movement of the oxidation reduction object included in the electrolytic solution of the electrolyte layer 5. Generally, the granularity of the eye of such a mesh shape electrode should just be within the limits of 20 to 500 meshes. When the granularity of the eye of a mesh shape electrode is more than 500 meshes, there is a possibility that movement of the oxidation reduction object included in an electrolytic solution may be checked. On the other hand, since problems, such as migration length becoming long by the time the electron poured into a semiconductor reaches a mesh shape current collection electrode, and causing increase of ohm loss, when the granularity of the eye of a mesh shape electrode is less than 20 meshes, arise, it is not desirable.

[0038]The structure of the perforated current collection electrode 4 will not be limited especially if it is the structure which the oxidation reduction object included in an electrolytic solution through the breakthrough of

an electrode can move. For example, the structure of the shape of a lattice which incorporated the laminated electrode material as shown in the mesh shape electrode structure or drawing 3 which arranged the electrode material of thin line state as shown in drawing 2 to mesh shape in all directions is employable.

[0039]In the case of the perforated current collection electrode 4 as shown in drawing 2 and drawing 3, a coloring matter support semiconductor layer can also be formed in a breakthrough by methods, such as the fluid depositing method, an electrolytic plating method, or an electroless deposition method. Distance which will move by the time the electron which could reduce the ohm loss of the current collection electrode, and was poured into the semiconductor by this reaches a current collection electrode can be shortened. As a result, the loss by the resistance produced when moving in the inside of a semiconductor can be reduced, and photoelectric conversion efficiency can be raised by leaps and bounds.

[0040]Since it is the same raw material as Pt film 9 of a counter-electrode when the perforated current collection electrode 4 is formed from Pt, the same reduction reaction will be performed on the surface of the perforated current collection electrode 4 as it is performed by the counter-electrode. For this reason, it is necessary to cover by a semiconductor coat so that the reduction reaction of the oxidant in an electrolytic solution may not advance in a perforated current collection electrode surface. In the case of a titanium oxide semiconductor coat, as a semiconductor coat forming method for such a purpose, methods, such as immersion to  $TiCl_4$  solution, electrolytic plating, electroless deposition, and the liquid phase depositing method, can be used, for example. As a semiconductor for covering a perforated current collection electrode surface, A kind of publicly known semiconductors, such as strontium tungstic acid, strontium titanic acid, 5 tungstic oxide, a 5 oxidation niobium besides titanium oxide, a cadmium sulfide, a zinc oxide, tin oxide, and 3 indium oxide, or two sorts or more can be used. In particular, the point of stability or environmental responsiveness to titanium oxide is preferred.

[0041]As mentioned above, when the perforated current collection electrode 4 is formed for the same raw material as a counter-electrode formation material, in order to prevent advance of the reduction reaction of the oxidant in the electrolytic solution in the perforated current collection electrode 4, it is necessary to cover the perforated current collection electrode 4 with a semiconductor coat but, and, Since the reduction reaction of the oxidant in an electrolytic solution does not occur in the perforated current collection electrode 4 when the perforated current collection electrode 4 is formed from a different raw material from a counter-electrode formation material, it is not necessary to cover the surface of the perforated current collection electrode 4 with a semiconductor coat.

[0042]When covering the surface of the perforated current collection electrode 4 with a semiconductor coat, this semiconductor coat can also be made to support sensitizing dye. In this case, the necessity of providing a coloring matter support semiconductor layer in a substrate face separately is lost.

[0043]In order to make small ohm loss by the perforated current collection electrode 4, the surface resistance of the perforated current collection electrode 4 is so good that it is low. As for the surface resistance of the perforated current collection electrode 4, it is preferred that it is below 50ohms / \*\*. The surface resistance value below 30ohms / \*\* is much more preferred. Although there is no restriction in particular in the lower limit of the surface resistance of the perforated current collection electrode 4, they are usually 0.1ohm/\*\*.

[0044]

[Example]Next, an example is given and this invention is illustrated concretely. However, this invention is not

limited only to the following example.

[0045]In the mixed liquor (capacity mixture ratio = 20/1) of the water and the acetylacetone containing example 1 surface-active agent, the titanium oxide particle (the product made by Japanese Aerosil, P25, mean particle diameter of 20 nm) was distributed at concentration about 2 wt(s)%, and slurry liquid was prepared. Next, this slurry liquid was applied on the 1-mm-thick glass substrate, and after the granularity of eyes laid the mesh shape Pt current collection electrode whose number is 200 and dried the coating film on the coating film further at 5 micrometers in thickness of the structure shown by drawing 2, it calcinated in 30-minute interspace mind at 500 \*\*. To said mesh shape Pt current collection electrode, the tunic of titanium oxide was covered beforehand. The titanium oxide film was formed by the liquid phase depositing method which consists of a mesh shape Pt current collection electrode being immersed in the water containing 2.0 g/L of fluorotitanium ammonium, and 1.2 g/L of boric acid, and neglecting it at 25 \*\* for 3 hours. Next, the porous-titanium-oxide film provided with this mesh shape Pt current collection electrode was immersed into the sensitizing dye solution expressed with  $[\text{Ru}(4,4'\text{-dicarboxyl } 2,2'\text{-bipyridine})_2\text{-(NCS)}_2]$  with a glass substrate, and coloring matter adsorption treatment was performed, flowing back at 80 \*\*.

[0046]The semiconductor electrode provided with the mesh shape Pt current collection electrode obtained as mentioned above and its counter-electrode were contacted to the electrolytic solution, and the optoelectric transducer was constituted. The electrolytic solution was closed with the semiconductor electrode provided with the mesh shape Pt current collection electrode, its counter-electrode, and a sealing agent. As a counter-electrode, the electrically-conductive-glass board ( $\text{F-SnO}_2$ , 10 ohm/sq, Asahi Glass make) with a thickness of 1 mm which formed Pt in 20-nm thickness was used. As an electrolytic solution, the mixed liquor (capacity mixture ratio = 80/20) of ethylene carbonate and acetonitrile containing tetrapropylammonium iodide (0.46M) and iodine (0.6M) was used. The mimetic diagram of the section structure of the dye sensitizing cell produced by making it above is shown in drawing 4. When the solar cell output when the xenon lamp was used for said solar cell and irradiated with the light of the illumination of  $450 \text{ W/m}^2$  was measured, photoelectric conversion efficiency was 7.1%.

[0047]In the mixed liquor (capacity mixture ratio = 20/1) of the water and the acetylacetone containing example 2 surface-active agent, the titanium oxide particle (the product made by Japanese Aerosil, P25, mean particle diameter of 20 nm) was distributed at concentration about 2 wt(s)%, and slurry liquid was prepared. Next, Pt current collection electrode of the shape of a lattice with a thickness of 20 micrometers of the structure shown by drawing 3 on a 1-mm-thick glass substrate in this slurry liquid was carried, and also it applied [ from ], the coating film was dried, and it calcinated in 30-minute interspace mind at 500 \*\*, and was considered as the form where titanium oxide membrane fills the inside of the lattice of a lattice-like Pt current collection electrode. The outside surface of this lattice-like Pt current collection electrode was beforehand covered with the titanium oxide film. This titanium oxide film immersed the lattice-like Pt current collection electrode in the water containing 2.0 g/L of fluorotitanium ammonium, and 1.2 g/L of boric acid, and formed it by the liquid phase depositing method which consists of neglecting it at 25 \*\* for 3 hours. Next, the porous-titanium-oxide film provided with this lattice-like Pt current collection electrode was immersed into the sensitizing dye solution expressed with  $[\text{Ru}(4,4'\text{-dicarboxyl } 2,2'\text{-bipyridine})_2\text{-(NCS)}_2]$  with a glass substrate, and coloring matter adsorption treatment was performed, flowing back at 80 \*\*.

[0048]The semiconductor electrode provided with the lattice-like Pt current collection electrode obtained as

mentioned above and its counter-electrode were contacted to the electrolytic solution, and the optoelectric transducer was constituted. The electrolytic solution was closed with the semiconductor electrode provided with the lattice-like Pt current collection electrode, its counter-electrode, and a sealing agent. As a counter-electrode, the electrically-conductive-glass board ( $\text{F-SnO}_2$ , 10 ohm/sq, Asahi Glass make) with a thickness of 1 mm which carried out 20-nm thickness membrane formation of the Pt was used. As an electrolytic solution, the mixed liquor (capacity mixture ratio = 80/20) of ethylene carbonate and acetonitrile containing tetrapropylammonium iodide (0.46M) and iodine (0.6M) was used. The mimetic diagram of the section structure of the dye sensitizing cell produced by making it above is shown in drawing 5. When the solar cell output when the xenon lamp was used for said solar cell and irradiated with the light of the illumination of  $450 \text{ W/m}^2$  was measured, photoelectric conversion efficiency was 7.4%.

[0049]By the liquid phase depositing method which consists of example 3 lattice-like Pt current collection electrode being immersed in the water containing 2.0 g/L of fluorotitanium ammonium, and 1.2 g/L of boric acid, and neglecting it for six days at 25 \*\*. 2-micrometer-thick titanium oxide membrane was formed in the lattice-like Pt current collection electrode surface, and it calcinated in 30-minute interspace mind at 500 \*\* after desiccation. Next, the titanium oxide membrane which covers this whole lattice-like Pt current collection electrode surface was immersed into the sensitizing dye solution expressed with  $[\text{Ru}(4,4'\text{-dicarboxyl } 2,2'\text{-bipyridine})_2\text{-}(\text{NCS})_2]$ , and coloring matter adsorption treatment was performed, flowing back at 80 \*\*.

[0050]The semiconductor electrode provided with the lattice-like Pt current collection electrode obtained as mentioned above and its counter-electrode were contacted to the electrolytic solution, and the optoelectric transducer was constituted. The electrolytic solution was closed with the semiconductor electrode provided with the lattice-like Pt current collection electrode, its counter-electrode, and a sealing agent. As a counter-electrode, the electrically-conductive-glass board ( $\text{F-SnO}_2$ , 10 ohm/sq, Asahi Glass make) with a thickness of 1 mm which carried out 20-nm thickness membrane formation of the Pt was used. As electrolytic solution liquid, the mixed liquor (capacity mixture ratio = 80/20) of ethylene carbonate and acetonitrile containing tetrapropylammonium iodide (0.5M) and iodine (0.04M) was used. The mimetic diagram of the section structure of the dye sensitizing cell produced by making it above is shown in drawing 6. When the solar cell output when the xenon lamp was used for said solar cell and irradiated with the light of the illumination of  $450 \text{ W/m}^2$  was measured, photoelectric conversion efficiency was 6.9%.

[0051]In the mixed liquor (capacity mixture ratio = 20/1) of the water and the acetylacetone containing example 4 surface-active agent, the titanium oxide particle (the product made by Japanese Aerosil, P25, mean particle diameter of 20 nm) was distributed at concentration about 2 wt(s)%, and slurry liquid was prepared. Next, this slurry liquid was applied on the 1-mm-thick glass substrate, and after carrying the mesh shape Au electrode of 200 meshes at 5 micrometers in thickness on the coating film and drying a coating film further, it calcinated in 30-minute interspace mind at 500 \*\*. Next, the porous-titanium-oxide film provided with this mesh shape Au electrode was immersed into the sensitizing dye solution expressed with  $[\text{Ru}(4,4'\text{-dicarboxyl } 2,2'\text{-bipyridine})_2\text{-}(\text{NCS})_2]$  with a glass substrate, and coloring matter adsorption treatment was performed, flowing back at 80 \*\*.

[0052]The semiconductor electrode provided with the mesh shape Au electrode obtained as mentioned above and its counter-electrode were contacted to the electrolytic solution, and the optoelectric transducer

was constituted. The electrolytic solution was closed with the semiconductor electrode provided with the mesh shape Au electrode, its counter-electrode, and a sealing agent. As a counter-electrode, the electrically-conductive-glass board (F-SnO<sub>2</sub>, 10 ohm/sq, Asahi Glass make) with a thickness of 1 mm which carried out 20-nm thickness membrane formation of the Pt was used. As an electrolytic solution, the mixed liquor (capacity mixture ratio = 80/20) of ethylene carbonate and acetonitrile containing tetrapropylammonium iodide (0.46M) and iodine (0.6M) was used. The mimetic diagram of the section structure of the dye sensitizing cell produced by making it above is shown in drawing 2. When the solar cell output when the xenon lamp was used for said solar cell and irradiated with the light of the illumination of 450 W/m<sup>2</sup> was measured, photoelectric conversion efficiency was 6.8%.

[0053]In the mixed liquor (capacity mixture ratio = 20/1) of the water and the acetylacetone containing comparative example 1 surface-active agent, the titanium oxide particle (the product made by Japanese Aerosil, P25, mean particle diameter of 20 nm) was distributed at concentration about 1 wt%, and slurry liquid was prepared. Next, the dry matter which applied this slurry liquid on the 1-mm-thick electrically-conductive-glass board (the Asahi Glass make, F-SnO<sub>2</sub>, 10 ohm/sq), and was obtained by drying was calcinated in 30 minutes and in the air at 500 \*\*, and the 10-micrometer-thick porous-titanium-oxide film was formed on the substrate. Next, coloring matter adsorption treatment was performed, having been immersed into the sensitizing dye solution expressed with [Ru(4,4'-dicarboxyl 2,2'-bipyridine)<sub>2</sub>-(NCS)<sub>2</sub>], and flowing back at 80 \*\* with the substrate which provided this porous-titanium-oxide film.

[0054]The semiconductor electrode obtained as mentioned above and its counter-electrode were contacted to the electrolytic solution, and the optoelectric transducer was constituted. In this case, as a counter-electrode, the electrically conductive glass which formed 20-nm Pt was used. The distance between two electrodes was 0.1 mm. As an electrolytic solution, the mixed liquor (capacity mixture ratio = 80/20) of ethylene carbonate and acetonitrile containing tetrapropylammonium iodide (0.5M) and iodine (0.04M) was used. When the solar cell output when the dye sensitizing cell produced by making it above was irradiated with the light of the illumination of \*\* 450 W/m<sup>2</sup> for xenon RAMPUWO was measured, photoelectric conversion efficiency was 5.2%.

[0055]

[Effect of the Invention]By arranging the semiconductor layer which supported coloring matter with this invention to the acceptance surface side of a current collection electrode, and using the current collection electrode of mesh shape or the shape of a lattice which has many breakthroughs as a current collection electrode, as explained above, When the electrolytic solution enabled it to contact a coloring matter support semiconductor layer via the breakthrough of this current collection electrode, it enables the light which entered from the acceptance surface to carry out a direct action to a coloring matter support semiconductor layer.

Therefore, the photoelectric conversion efficiency of an optoelectric transducer (for example, solar cell) can be raised by leaps and bounds.

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[Translation done.]